

Effect on thermal oxidation in TiO₂ nanostructures on nanohardness and corrosion resistance

Efecto de la oxidación térmica en nanoestructuras de TiO₂ sobre la nanodureza y resistencia a la corrosión

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ABSTRACT

This article aimed to analyze the effect of the thermal oxidation in the corrosion resistance and the hardness properties of TiO₂ nanostructures obtained by the anodizing process in the HF/H₃PO₄ solution. TiO₂ nanostructures on Ti6Al4V obtained by anodizing processes were subjected to thermal oxidation (TO) treatments over a temperature range from 500 °C to 620 °C for 2 hours. Surface morphology was evaluated by using scanning electron microscopy; the hardness properties of TiO₂ nanostructures were obtained by Nanoindentation measurements using a Berkovich probe with a tip radius of 150 nm. The corrosion behavior of the samples was studied using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The results showed that TiO₂ nanostructures, modified by thermal oxidation, increased the surface properties of hardness and corrosion resistance, compared to the substrate, maintaining its mixed or tubular structure. On the other hand, a transformation of nanotubes to nanopores after 600 °C was evidenced, generating significant changes in the mechanical properties of these structures.

Keywords: Nanostructures, TiO₂, nanohardness, EIS, thermal oxidation.

RESUMEN

El objetivo de este artículo es analizar el efecto de oxidación térmica en la resistencia a la corrosión y las propiedades de dureza de nanoestructuras de TiO₂ obtenidas por procesos de anodizado en solución de HF/H₃PO₄. Las nanoestructuras de TiO₂ sobre Ti6Al4V por procesos de anodizado fueron sometidas a tratamiento de oxidación térmica (OT) en un rango de 500 °C a 620 °C por dos (2) horas. La morfología superficial fue evaluada mediante microscopia electrónica de barrido; las propiedades de dureza de nanoestructuras de TiO₂ fueron obtenidas por medidas de nanoindentación usando una probeta Berkovich de radio 150 nm. El comportamiento a la corrosión de las muestras fue estudiado usando polarización potenciodinámica y espectroscopia de impedancia electroquímica (EIS). Los resultados mostraron que la nanoestructuras de TiO₂, modificadas por oxidación térmica, incrementaron las propiedades superficiales de dureza y resistencia a la corrosión, comparadas a las del substrato, manteniendo su estructura mixta o tubular. Además, se evidenció una transformación de nanotubos a nanoporos después de 600 °C generando cambios significativos en las propiedades mecánicas de estas estructuras.

Palabras clave: Nanoestructuras, TiO₂, nanodureza, EIS, oxidación térmica.

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INTRODUCTION

The use of titanium alloys in the medical field has responded very well due to its properties of biocompatibility, corrosion resistance, low elastic modulus compared to stainless steels or cobalt-based alloys [1-4]. However, it has been found that chloride ions present in the different extracellular of body fluids such as blood and interstitial fluids generate significant corrosion in this type of material [5-8]. Processes of superficial modification, such as anodizing and thermal oxidation, have provided a solution to tribological and corrosion problems present in this type of alloys [9-11]. Anodizing is a method of superficial modification that produces different types of oxide films in the metal, either barrier-type films or nanostructured films [12-13]. Some the electrolytes used for the formation of these structures are the different diluted solutions of sulfuric acid, phosphoric acid, acetic acid, among others [14]. For the formation of nanotubes, it is essential that the electrolyte used in the anodizing process of titanium contains fluoride ions [15] which allow generating the pits of the oxide layer in formation, thus, facilitating the kinetic growth process of TiO₂ nanotubes [16]. In addition, it is necessary to apply a constant potential using a DC power supply to ensure the homogeneity of nanotubes [17-18].

Self-organized TiO₂ nanotubes films, generated from anodizing processes, have allowed a greater interaction with cell tissue due to their nature, compared with barrier-type films. However, it is known that the mechanical properties of these structures should be analyzed and studied depending on the type of application used, making necessary the development of treatments that allow improving their mechanical properties at a nanometric level [19-22]. According to some researches, the development of anodized films allows a better bioactive surface behavior with increased cellular adhesion; however, the mechanical resistance or the tribological behavior of these films is limited [23-26]. TiO₂ exists in three phases: anatase, brookite and rutile; however, anatase and rutile are the phases of major study in most of the biomedical applications [27], particularly for orthopedic and osteosynthesis applications due to the high surface reactivity, which in turn depends on the crystallinity [10, 21, 28].

Thermal oxidation of titanium and its alloys has already been investigated for different biomedical

applications with the aim of improving its hardness and wear resistance [10]. The passive behavior of the oxide film generated by thermal oxidation plays an important role for its suitability as an implant material. Likewise, it reduces the kinetics of the corrosion process by blocking the diffusion of the aggressor ions present in the body fluids of the surface of the metal [29]. Corrosion behavior is one of the most important characteristics for the application of implants; therefore, the corrosion resistance of nanotubes should be investigated before being used in clinics [30].

The manufacture of self-organized layers of oxide nanotubes as a suitable surface treatment can improve the mechanical characteristics and corrosion resistance of titanium alloys. In terms of corrosion resistance, the layers of TiO₂ nanotubes on titanium have a better resistance in the simulated biofluids compared to Ti without being modified [31-33]. The growth of nanostructures in titanium alloys Ti6Al4V, as well as the development of modification treatments, has been a subject of great interest in terms of their adhesion properties, corrosion resistance, biocompatibility, and wear resistance [14]. However, the study of mechanical properties of these nanostructures remains being a subject of study due to the different variables that might be modified to improve their development (type of electrolyte, time, type of surface modification, voltage, current density, and structure obtained). Some authors have reported hardness values that vary from 0.7 GPa to 12 GPa depending on the load and assay condition [21-22, 34-35].

Therefore, the objective of this article is to analyze the effect of thermal oxidation on corrosion resistance and hardness properties of TiO₂ nanostructures obtained by anodizing process in the HF/H₃PO₄ solution.

MATERIALS AND METHODS

In this investigation, Ti6Al4V ELI alloy (ASTM F136) discs with 12.7 mm diameter and 3 mm of thickness were used. Before subjecting to anodizing and thermally oxidation process, the samples were ground with different grades of SiC papers (grit size 240 up to 1500) and then polished with diamond pastes of 3 and 1 μm average particle size. Finally, the samples were ultrasonically cleaned in ethanol for 10

minutes and air-dried at room temperature. Anodization (AN) was carried out in an electrochemical cell with a two-electrode configuration [36]. Ti6Al4V ELI discs were used as anode and stainless-steel plate as cathode. The anodization was conducted at room temperature. A constant potential of 14V was applied using a DC power supply. The electrolytic solution of 1 M H_3PO_4 + 0.2% v/v HF was used to obtain nanotube morphology. The distance between anode and cathode was maintained at a constant distance of 2 cm. All of samples were anodized for about 1 hour and then rinsed with distilled water and air-dried at room temperature.

Based on a literature review and taking into account the studies of Sarraf, Zalnezhad, Bushroa and Hamouda [37], Deen, Farooq, Raza and Haider [32] and Bessauer *et al.*, the relationship between variables for the anodization on the Ti6Al4V alloy was determined. After anodizing, thermal oxidation (TO) treatments were carried out in a muffle furnace over range temperatures from 500 °C to 620 °C for 2 hours, and subsequently furnace cooled. The heating rate was approximately 5 °C/min. The morphology of the samples was observed by scanning electron microscopy (SEM), using a scanning electron microscope model Quanta FEG 650 equipped with X-ray dispersive spectroscopy EDX (Apollo X). Data of nanotube diameters for different samples, were obtained using image J software and expressed as mean \pm standard deviation (SD) and were statistically analyzed by Statgraphics software; values of $p < 0.05$ were considered significant.

Morphological exams of the corresponding surfaces were performed as part of the microstructural characterization, through optical profilometry and using an Ultra Precision 3D Profilometer Talysurf CCI. Additionally, nanoindentation test were carried out using the triboindenter TI 950 (Hysitron INC.) An array of 10X10 indentations was performed by applying a force of 500 mN using a Berkovich type indenter. Electrochemical studies were conducted using a Potentiostat/Galvanostat Autolab PSGTAT 302 with impedance module FRA2 (frequency response analyzer). A microcell was used to evaluate the different regions of each sample, with an area of 0.031 cm². Three tests were performed for each condition. The conventional three electrode cell was used to carry out the electrochemical studies. The tests were conducted in Ringer's solution (8.4 g/L

NaCl, 0.302 g/L KCl, 0.298 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.15 g/L NaHCO_3) which simulates human body fluid at 25 ± 2 °C, with pH of 7.3 ± 1.0 . Ti6Al4V was kept as the working electrode; Pt wire and Ag/AgCl (KCl sat) were used as counter and reference electrodes, respectively. Impedance spectroscopy (EIS) measurement was carried out in the frequency range of 10⁵ Hz to 10⁻² Hz with an excitation voltage of 10 mV (peak-to-peak). The measurements were initiated after 2 hours of open circuit potential. After EIS measurements, potentiodynamic polarization studies were carried out from -250 mV to +1200 mV (versus open circuit potential) at a scan rate of 1 mVs⁻¹.

RESULTS AND DISCUSSION

MICROSTRUCTURAL AND TOPOGRAPHIC CHARACTERIZATION OF TiO₂ NANOTUBES

Morphology of nanostructures

The Figure 1 shows the morphology of the TiO₂ nanostructures obtained by combined processes of anodizing and thermal oxidation at temperatures from 500 °C to 620 °C. Figure 1a shows the formation of TiO₂ nanostructures to 14V obtained by electrolytic anodizing; in the surface a uniform and orderly distribution of nanotubes is observed with average diameters of 66.9 ± 7.6 nm, similar data were found by Mohan, Anandan and Rajendran [39].

Figures 1b, 1c, 1d, 1e and 1f show TiO₂ nanostructures of the anodized and thermally oxidized samples at 500, 540, 580, 600 and 620 °C respectively. Figures 1b, 1c and 1d exhibit a self-aligned and randomly disordered TiO₂ nanotubes with a resulting average diameter of 62.59 nm and 61.52 nm, respectively. A change of morphology with a deformation and enclosure of the nanotubes was seen, with a densification effect of the nanotube film; effect that is generated by submitting the samples to processes of thermal oxidation, thus, improving the mechanical properties as expressed by Sarraf, Zalnezhad, Bushroa and Hamouda [37]. In addition, it was observed that small crystalline structures were formed from 600 °C, covering the nanostructures, which was more evident in the thermally oxidized sample at 620 °C, as shown in previous studies [25].

Table 1 shows the diameters of the nanostructures obtained. It shows a diameter growth from 500 °C to 560 °C, however after 580 °C a slight decrease in

the nanotube diameter was observed after thermal oxidation, as indicated by Munirathinam and Neelakantan [21], which can be attributed to the sintering occurred by the crystallization effect. A transformation of nanotubes to nanopores occurred after 600 °C, the transformation that is also evidenced by other authors such as Sarraf, Zalnezhad, Bushroa and Hamouda [37] and Mohan, Anandan and Rajendran [39], where the increase in temperature caused significant changes in microstructures, making the nanotubes to collapse completely and adopt compact film morphology of TiO₂ (as shown in Figure 1e and 1f). The structure on the nanopores is recognized because there is no intertubular space between them, as evidenced by nanotubes.

Bauer, Park, Von Der Mark and Schmuki [40] using 1M concentrations of H₃PO₄ with different concentrations of HF, found self-organized nanostructures as presented in this research, however with a smaller nanotube diameter due to the absence of heat treatment.

Roughness measurements of nanostructures

Figure 2 shows 3D topography of nanostructured and thermally modified samples and surface roughness obtained from an optical profilometry. The roughness values are represented in terms of Ra (arithmetic mean deviation of the roughness profile), Rq (middle square root of the roughness), Rku (kurtosis), Rp (maximum peak height of the roughness profile), Rv (maximum valley depth of the roughness profile)

Table 1. Nanostructure diameter obtained by anodizing and thermal oxidation.

Sample	Diameter (nm)	Sample	Diameter (nm)
AN	66.93 ± 7.68	AN+TO560 °C	65.24 ± 6.13
AN+TO500 °C	59.71 ± 6.74	AN+TO580 °C	61.52 ± 5.36
AN+TO520 °C	63.04 ± 7.70	AN+TO600 °C	51.91 ± 5.85
AN+TO540 °C	62.59 ± 5.35	AN+TO620 °C	57.41 ± 7.10

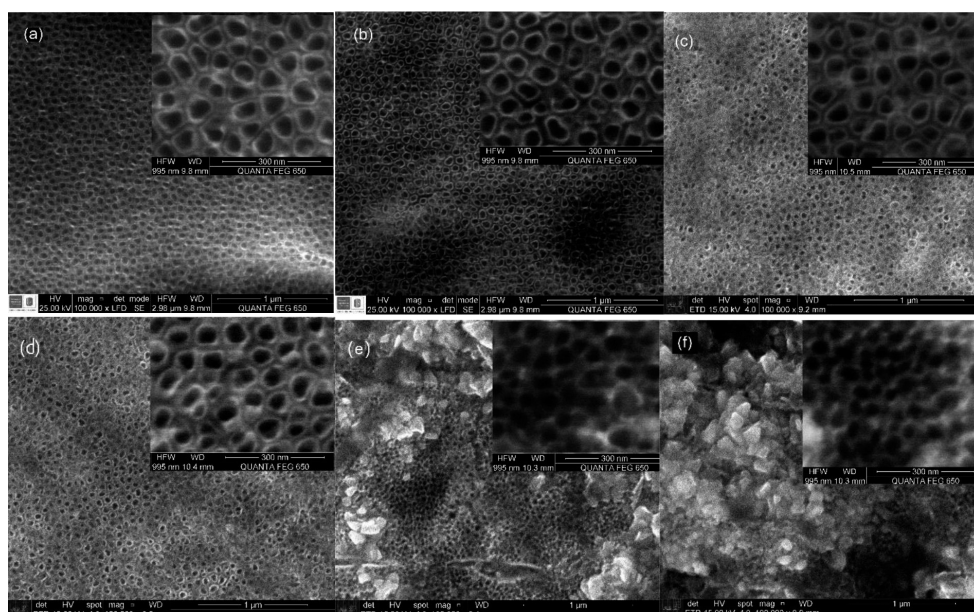


Figure 1. Surface Morphology of the nanostructures of titanium obtained by thermal oxidation treatment for temperatures between 500 °C and 620 °C on TiO₂ nanostructures samples on Ti6Al4V. a) AN, b) AN+TO500 °C, c) AN+TO540 °C d) AN+TO 580 °C, e) AN+TO 600 °C f) AN+TO 620 °C. AN = Anodized, TO = Thermally oxidized. Treatment time: 120 minutes.

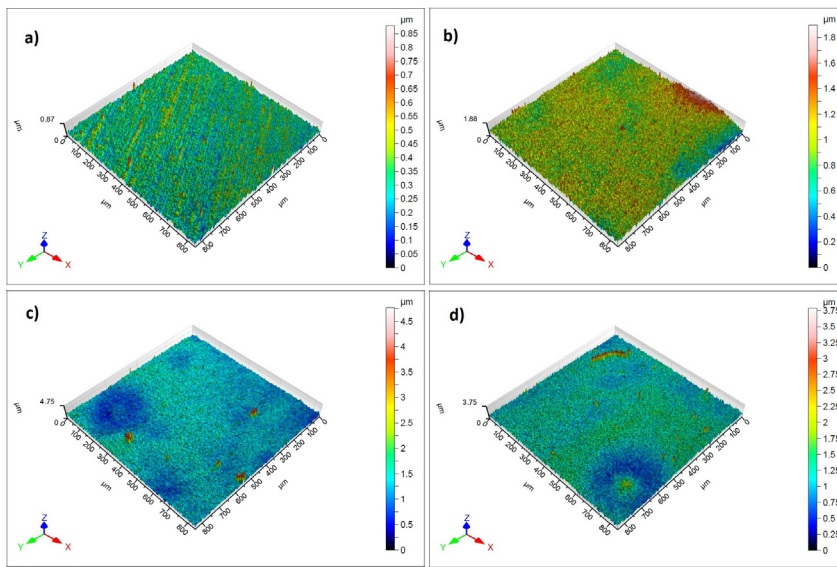


Figure 2. Surface Morphology of nanostructured and thermally modified samples. a) Substrate -Ti64 b) AN+TO500 °C, c) AN+TO560 °C, d) AN+TO620 °C.

Table 2. Roughness parameters.

Samples	Ra (μm)	Rp (μm)	Rv (μm)	Rq (μm)	Rku	Rsm (μm)
Substrate-Ti64	0.030	0.149	0.206	0.036	2.140	5.480
AN+TO500 °C	0.146	0.423	0.876	0.178	2.480	6.370
AN+TO520 °C	0.108	0.404	0.660	0.145	3.137	5.200
AN+TO540 °C	0.107	0.435	0.443	0.132	2.713	5.340
AN+TO560 °C	0.117	0.422	0.476	0.144	2.680	4.930
AN+TO580 °C	0.146	0.423	0.876	0.178	2.488	6.370
AN+TO600 °C	0.139	0.619	0.876	0.174	2.662	7.200
AN+TO620 °C	0.224	0.709	0.860	0.294	3.980	11.700

and Rsm (mean spacing of the roughness profile). (See Table 2). Figure 2a presents an orderly and uniform surface of the substrate; this also shows the change of surface as the temperature increased as demonstrated in Figures 2b, 2c, 2d.

The increase in the temperature allowed observing an increment of the roughness, represented in Ra values from 0.14 μm to 0.22 μm for 500 °C and 620 °C respectively, compared to Ra values of 0.03 μm of the substrate. According to Biswas, Manna, Chatterjee, Bhattacharyya and Majumdar [41], this increase in roughness could favor cellular adhesion in relation to very smooth surfaces, possibly due to the increase of water in the surface, as was reported in previous studies [36]. Guéhenne, Soueidan, Layrolle and

Amouriq [42] found that the roughness increment in the surface favors the biomechanical stability and the osseous anchorage of the implants subjected to superficial treatments. Rp values remained constant between 500 °C and 580 °C, but with a lower temperature the values increased from $0.4 \pm 0.02 \mu\text{m}$ to $0.7 \mu\text{m}$ by the transformations present and the formation of titanium oxides.

In general, the values of Rku (kurtosis) were lower than 3, showing that the distribution of the peaks had a Gaussian tendency, similar data were found by Gadelmawla, Koura, Maksoud, Elewa and Soliman [43]. The average spacing between the peaks increased from 560 °C, Rsm, compared to the one observed in low temperature samples; meanwhile, Rv value

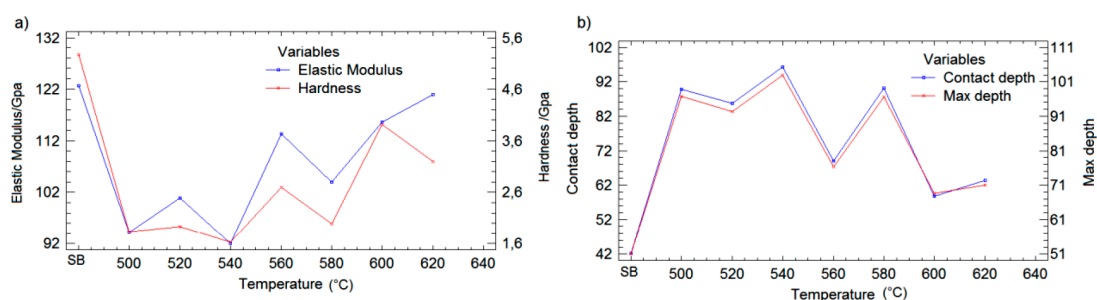


Figure 3. Variation in a) hardness and elastic modulus, b) contact depth and maximum penetration depth as a function of thermal oxidation temperature.

of anodized and thermally oxidized samples was greater than the R_v value of substrate.

NANOMECHANIC PROPERTIES

Figure 3a shows the comparison of the elastic modulus with the hardness for the substrate and thermally modified samples (nanostructures TiO₂ film) between 500 °C and 620 °C, and figure 3b corresponds to the contact depth and maximum penetration depth depending on the temperature.

It was found that, with the increase in temperature, hardness and elastic modulus values of the nanostructures TiO₂ film, were increasing from 1.8 ± 0.7 to 3.2 ± 0.8 for 500° and 620 °C respectively. Similarly, elastic modulus values increased from 94GPa to 120GPa for the same temperatures. Hardness and elastic modulus values for nanostructures TiO₂ film were lower than those of the substrate (5.2 GPa and 122GPa), similar behavior that was found by other authors [22, 31].

The lowest contact depth and maximum depth values for the substrate and the samples treated at 600 and 620 °C correspond to the maximum hardness values 5.2, 3.9 and 3.1 GPa respectively. On the other hand, it was found that the elastic modulus values of the modified surfaces did not exceed the value of the elastic modulus of the substrate, which reduced the efforts between the substrate and the coating and improved the behavior of the surfaces.

ELECTROCHEMICAL RESPONSE

Potentiodynamic tests

Potentiodynamic curves for thermally oxidized samples at different temperatures and substrate

of Ti6Al4V are shown in Figure 4. Polarization curves, in all cases, went from an active behavior to a passive behavior, which is typical of this type of materials [30, 38, 42].

The highest current density was presented in the substrate showing a higher dissolution rate; On the other hand, the nanostructures of TiO₂ exhibited a passive behavior with low current densities. It was found that the samples subjected to 540 °C, 560 °C and 600 °C presented the lowest corrosion rate (V_{corr}), however all the TiO₂ nanostructures showed a lower corrosion rate compared to the substrate, due to the applied heat treatment. In addition, the nanostructures showed a good performance in media containing Cl⁻ ions, because no pits were found on the surface, during and after the potentiodynamic tests performed. The corrosion potentials (E_{corr})

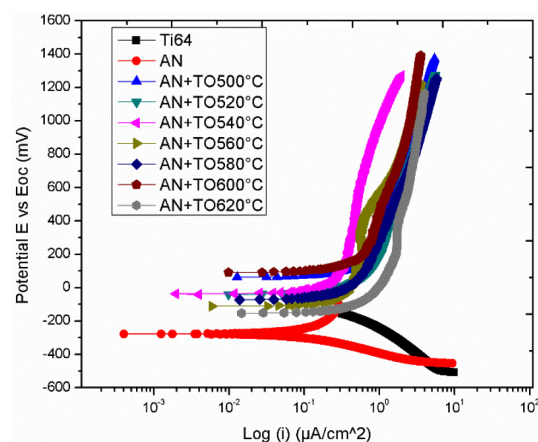


Figure 4. Potentiodynamic curves for thermally oxidized samples at different temperatures. AN = Anodized, TO = Thermally oxidized.

of the TiO_2 nanostructures presented more positive potentials compared to the substrate and anodized material (Table 3).

Electrochemical Impedance Spectroscopy

Figure 5 shows the Bode diagrams a) phase angle and b) impedance against frequency, which had variations in relation to the substrate and the thermally oxidized and anodized samples. The phase angle diagram in Figure 5a presents in low frequency areas (0.01 Hz-100 Hz) a phase angle that went from 20° to 70° for the substrate, compared to the anodized material that showed a reduction in the rank from 55° to 45° . At high frequencies, the substrate presented a lower angle compared to the anodized and thermally oxidized material. Nanostructured TiO_2 sample at 620°C was the one that presented the highest angles at high frequencies. On the other hand, the maximum phase angle was presented

in the substrate, typical aspect of passive films formed on the surface [39, 45]. EIS response of the nanostructured TiO_2 sample to 620°C , showed two time constants: one at low frequency (0.01 Hz) and another at high frequency (1000Hz) with possible double layer formation; the first generated by the initial anodizing layer and the second by the thermal oxidation process [46].

Figure 5b presents the impedance graph for the different studied temperatures, indicating that the nanostructured samples showed high impedance at high frequencies compared to the substrate. In the case of the substrate, a section of horizontal straight line was found at high frequency, consequence of the resistance to the electrolyte, which is a very similar behavior for thermally oxidized samples above 580°C . In addition, samples anodized and thermally oxidized at 540 , 560 and 620°C show

Table 3. Corrosion potentials (E_{corr}), corrosion current density (I_{corr}) and Corrosion rate (V_{corr}) of tested samples.

Sample	E_{corr} (mV)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	V_{corr} (mpy)
Ti64	-99.220	0.3924	3.455E-03
AN	-278.300	0.1807	1.591E-03
AN+TO500 $^\circ\text{C}$	59.204	0.2313	2.037E-03
AN+TO520 $^\circ\text{C}$	-43.447	0.2530	2.227E-03
AN+TO540 $^\circ\text{C}$	-42.907	0.1585	1.395E-03
AN+TO560 $^\circ\text{C}$	-114.410	0.1811	1.595E-03
AN+TO580 $^\circ\text{C}$	-75.012	0.2382	2.097E-03
AN+TO600 $^\circ\text{C}$	85.906	0.2067	1,820E-03
AN+TO620 $^\circ\text{C}$	-155.731	0.4017	3,536E-03

*AN = Anodized, TO = Thermally oxidized.

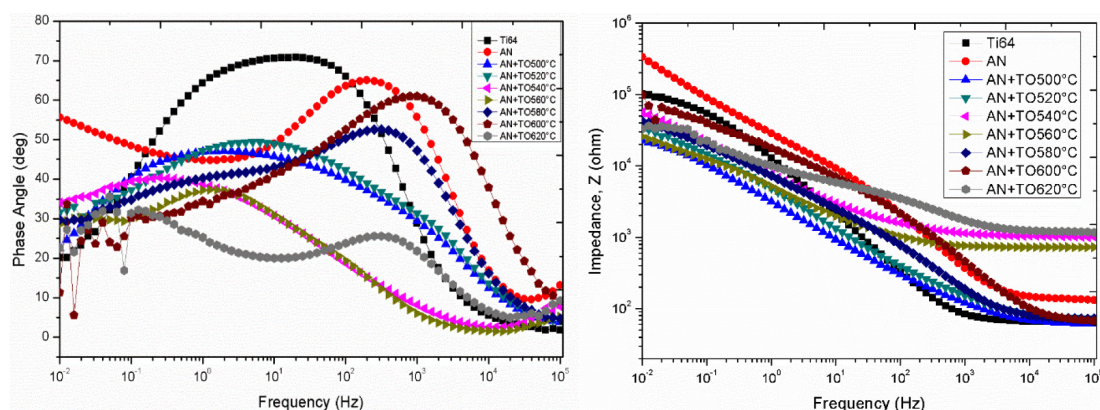


Figure 5. Bode diagrams, a) phase angle and b) impedance depending on the frequency in logarithmic scale.

higher values of impedance at high frequencies, caused by a difference in the values of resistance to the solution, this can be due to the absorption of species by the nanostructures, which manages to generate an increase in the electrical resistance of the Ringer's solution. This species absorption indicates that the nanostructured TiO₂ surfaces are highly reactive compared to the untreated alloy [36].

In relation to nanostructured and thermally oxidized samples, it was found that the best treated sample condition was the one developed at 620 °C, where high impedance was shown at low frequencies compared with other thermally oxidized samples. Y. Liu and J.Chen *et al.*, reported that, in some cases, modified samples showed inflection points that demonstrated variants of time, making possible a mass transfer and generating a different behavior both for the base as for the walls of the nanotube, presenting a diffusion process in the film [47-48]. Figure 6 shows the equivalent circuits used to model the behavior of the substrate, anodized samples and the anodized and thermally oxidized samples.

In the model applied to anodized and thermally oxidized samples, R1 was the resistance to the solution, R2 and R3 were the resistance of the internal barrier and the outer layer; W was the Warburg impedance and CPE1 and CPE2 were the constant phase elements. The resistance of the internal barrier

layer corresponded to the polarization resistance of the film, while the resistance of the outer layer corresponded to the load transfer resistance of the film. CPE1-P and CPE2-P elements indicated the TiO₂ solution-nanotubes interface and TiO₂-substrate nanotubes, respectively. The values obtained for CPE1-P indicated a highly capacitive behavior associated with the opposition to the load transfer generated by the TiO₂ nanostructures and the titanium oxide formed naturally. On the other hand, the values for CPE2-P, demonstrated a resistive-capacitive behavior, which can be associated with the morphology of that interphase. Table 4 shows the values of the equivalent circuit elements for the different samples. Chi squared (χ) parameter was used for the curve parameter, where values of 10⁻³ and 10⁻⁴ were found.

Thermal oxidation processes in untreated titanium alloys (Ti6Al4V) generated crystalline structures of anatase and rutile, especially after 600 °C, where a transformation of amorphous to crystalline structures was evidenced, which increased the surface hardness of the coating, as it was shown in previous works [49]. However, it has been found that nanotubular structures, subjected to thermal oxidation processes, not only favor cell growth, according to previous studies [50-51], but also improve the mechanical properties (hardness) in this type of nanostructures, generating alternatives for possible tribological applications.

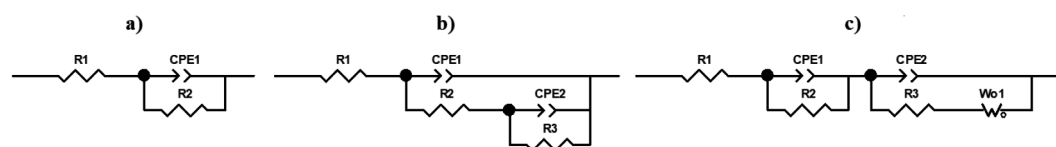


Figure 6. Equivalent circuits to adjust the impedance data for a) Substrate Ti6Al4V b) Anodized samples to 14V, AN, and c) anodized and thermally oxidized samples, AN+TO.

Table 4. Values of the equivalent circuit elements for the different samples.

Element	Ti64	AN	AN+TO500 °C	AN+TO540 °C	AN+TO580 °C	AN+TO620 °C
R1	62.73	131.4	57.55	979.7	69.53	1117
CPE1-P	0.8119	0.8569	0.8271	0.5933	0.7800	0.6293
R2	1.03E+05	9052	33.25	63309	908.7	4899
CPE2-P		0.5234	0.5685	0.4535	0.7695	0.8324
R3		5.35E+13	2.10E+04	46431	36497	30254
W01-P			0.3160	0.46537	0.30686	0.33527
Squared Chi	0.0087325	0.0001410	0.0002589	0.0013290	0.0004011	0.0087045

On the other hand, in this investigation, thermal oxidation processes below 620 °C and applied to TiO₂ nanostructures, increased surface roughness, reduced the corrosion rate and maintained a tubular and organized structure, which favors the use for different applications in biomedical implants.

CONCLUSIONS

SEM images showed that nanotubular arrays were completely transformed into nanopores after 600 °C and that the coarsening of the TiO₂ nanotube arrays occurred at temperatures higher than 580 °C

The thermally oxidized and anodized samples showed a passive behavior with low current densities compared to the substrate, being the samples AN+TO600 °C and 620 °C the ones with the best electrochemical behavior.

The oxidized samples at 620 °C had, in the equivalent circuits, two-time constants with possible double-layer formation, an internal barrier and an external porous-type of the oxide film, indicating a resistive-capacitive behavior, both in the base as in the walls, presenting a diffusion process in the film formed. Additionally, there was an increment in the roughness (Ra) that was favored by the increase in temperature, making structures friendlier with the cell tissue.

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